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Outstanding visible photocatalytic activity of a new mixed bismuth titanatate material

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ABSTRACT

In this work, a new photocatalyst based on bismuth titanates with outstanding visible photocatalytic activity was prepared by a facile hydrothermal method. The synthesised material showed visible activity as high as UV activity of commercial TiO_2 P25 under the same experimental conditions for phenol degradation. A wide characterisation of the photocatalyst was performed. The material was composed of three phases; majority of $Bi_{20}TiO_{32}$ closely interconnected to $Bi_4Ti_3O_{12}$ and amorphous TiO_2. The high visible activity showed by this material could be ascribed to a combination of several features; i.e. low band gap energy value (2.1 eV), a structure allowing a good separation path for visible photogenerated electron-holes pairs and a relatively high surface area. This photocatalyst appeared as a promising material for solar and visible applications of photocatalysis.

1. Introduction

Titanium dioxide (TiO_2) has been until now the most studied material used as photocatalyst, due to its good properties such as nontoxicity, chemical and photochemical stability and remarkable photoactivity under ultraviolet irradiation [1,2]. However, there are also some drawbacks of this material which hinder its wide use for many applications; mainly its high recombination rate of photogenerated electron-holes which lower its photoefficiency and its inability to be active under visible light. Due to its large band-gap TiO_2 can only absorb light in the ultraviolet region which limits its implementation for solar and indoor applications [3]. Thus, in the last years, a lot of effort in the photocatalysis research has been focused in the development and preparation of alternative materials to TiO_2 for solar and visible photocatalytic applications [4–6]. In this sense the searching of new or modified materials with absorption in the visible range of the spectrum has been a deal in many studies with the objective of obtaining materials with also a lower recombination rate of photogenerated charges for getting higher efficiency in the photocatalytic processes [4–8].

In this context, the family of bismuth titanates has attracted the interest of researchers in the area due to promising positive results in visible photocatalysis. Bismuth titanates include several different phases such as $Bi_2Ti_2O_7$, $Bi_2Ti_4O_{11}$, $Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$, $Bi_{20}TiO_{32}$, etc. [9]. Probably the most studied phase, for photocatalytic applications, is the $Bi_4Ti_3O_{12}$, which has shown high or moderate photocatalytic activity under visible illumination in several studies [10–15]. Although the phase $Bi_{20}TiO_{32}$ has also appeared as photoactive, it has been much less studied due to its metastable character, which makes it difficult to obtain as single phase or by means of mild conditions preparation methods. The visible activity of $Bi_{20}TiO_{32}$ is ascribed to the hybridized valence band by Bi6s and O2p orbitals which lead to a low band gap value [16]. This phase has been mainly obtained by synthetic procedures involving severe conditions as quenching methods at high temperatures [17–20]. This kind of preparation methods usually gives low surface areas and highly irregular materials, which in principle are negative features for catalysts. Therefore, when these materials are expected to be used as photocatalysts it would be worth to study alternative synthetic methods to get this kind of materials using mild preparation conditions [20].

In this paper, materials based in Bi-Ti-O have been prepared with an extraordinary activity in the visible, evaluated in the phenol photodegradation reaction. This model compound was chosen due to its wide utilisation in environmental photocatalytic studies [21,22]. Additionally, as visible activity was also evaluated, it appears as more appropriate substrate than dies, which have been also often used but that could present photosensibilisation effects masking real visible activity [23].

A wide characterization has been performed in order to understand the good visible photocatalytic performance. As reference material TiO_2 Degussa P25 was used and it was observed that the

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Table 1
Some characterisation results for the different photocatalysts.

	Crystalline phases (XRD)	Bi/Ti Content (molar, XRF)	S_{BET} (m^2/g)	Band Gap (eV)
BTO_Fresh	100% $Bi_4Ti_3O_{12}$	1.47	46	2.9
BTO_400	23% $Bi_4Ti_3O_{12}$ 77%$Bi_{20}TiO_{32}$	1.47	35	2.1
TiO2 P25	80% TiO_2 Anatase 20% TiO_2 Rutile	–	50	3.1

visible activity of the obtained Bi-Ti-O material was comparable to the activity of TiO_2 P25 under the ultraviolet illumination under the same experimental parameters. This, as far as we know, has not often been reported. The materials obtained are then very promising for any kind of solar application and/or indoors application, where visible light would be the source of illumination.

2. Experimental

2.1. Catalysts preparation

The Bi-Ti-O sample was prepared by mixing two solutions with the corresponding precursors and a further hydrothermal treatment.

First solution (solution A) was obtained by mixing Titanium tetraisopropoxide (TTiP Aldrich 97%) in Isopropanol (Aldrich 99.9%) and distilled water. This solution was kept under stirring at room temperature for one week to obtain a milky sol, as described in a previous paper [24].

Second solution (solution B) was prepared by dissolving $Bi(NO_3)_3 \cdot 5H_2O$ (analytical grade from Aldrich) in glacial acetic acid (reactive grade from Aldrich) to obtain a 1 M solution.

Then, solution B was slowly added to solution A and kept under stirring for one hour. Afterwards, triethylamine (TEA, Aldrich >99.5%) was added until reaching a pH value of 9. The resulting sol was transferred into a Teflon recipient inside of a stainless steel autoclave and hydrothermal treatment was performed at 140 °C for 20 h. A precipitate was obtained and was then filtered, repeatedly washed with distilled water and dried overnight at 120 °C.

The obtained powder was divided in two portions; one of them was calcined at 400 °C for 2 h. Hereafter, the non-calcined sample is named as BTO-Fresh, and the calcined one BTO-400.

On the other hand, commercial TiO2 Degussa P25 was employed "as received" without previous treatment.

2.2. Characterisation of the catalysts

Crystalline phase composition and degree of crystallinity of the samples were estimated by X-ray diffraction (XRD), on a Siemens D-501 diffractometer with Ni filter and graphite monochromator using Cu Kα radiation (0.15406 nm).

Global composition was determined by X-ray fluorescence spectrometry (XRF) in a Panalytical Axios sequential spectrophotometer with a rhodium tube as the source of radiation. XRF measurements were performed onto pressed pellets (sample included in 10 wt% of wax).

BET surface area and porosity measurements were carried out by N_2 adsorption at 77 K using a Micromeritics 2010 instrument.

The morphology and microcharacterization of the samples were analysed using scanning (SEM) and transmission (TEM) electron microscopy techniques. The samples were dispersed in ethanol using an ultrasonicator and dropped on a carbon coated copper grid. For SEM observations, a Hitachi S 4800 field emission-SEM was used in secondary electron mode at an acceleration voltage of 5 kV with an EDX detector for chemical analysis. The samples were sufficiently conductive, thus they were not coated with any conductive material in order to avoid charging artefacts.

For TEM studies, a FEI TECNAI G2 F30 S-twin high resolution transmission electron microscope (HRTEM) was used, with field emission gun (FEG) and scanning-transmission capabilities (STEM) operating at 300 kV and 0.2 nm point resolution. The microscope was equipped with a high angle annular dark field (HAADF) detector with 0.16 nm point resolution from Fischione Instruments, and an INCA X-Max 80 silicon drift detector (SDD) for the energy dispersive X-ray analysis (EDX). The Gatan Digital Micrograph software (Gatan Inc.) was used to measure lattice spacing and to calculate the First Fourier Transform (FFT) and the Java version Electron Microscope Software (JEM) was used to analysed the different phases of the samples. The analysis of the HAAD-STEM images and the EDX spectra profile were done with the ES Vision software (FEI Company).

UV–vis spectra were recorded by using a Cary 100 (Varian) in the diffuse reflectance mode (R) and transformed to a magnitude proportional to the extinction coefficient (K) through the Kubelka–Munk function, $F(R\infty)$. Samples were mixed with $BaSO_4$ that does not absorb in the UV–vis radiation range (white standard). Scans range was 240–800 nm.

2.3. Photocatalytic activity

The photocatalytic activity of the samples was evaluated in the phenol oxidation reaction using a batch reactor (250 ml) and an Osram Ultra-Vitalux lamp (300 W) with sunlike radiation spectrum. A concentration of 1 g/L of photocatalyst was used and the initial concentration of phenol was 50 ppm.

The intensity of the incident UVA light on the solution was measured with a PMA 2200 UVA photometer (Solar Light Co.) being ca. 90 W/m^2 (UVA PMA2110 sensor; spectral response 320–400 nm). On the other hand, the intensity of light in the visible range measured in this case was 110 W/m^2 (Photopic PMA21300 sensor; spectral response 400–700 nm). The photocatalytic runs in the visible range were performed by using a polyester UV filter sheet (Edmund Optics) showing 99.9% of absorbance below 390 nm.

In the oxidation tests, an oxygen flow was employed what produces a homogenous suspension of the catalyst in the solution. Before each experiment, the catalysts were settled in suspension with the reagent mixture for 20 min to allow catalyst-phenol adsorption equilibration.

The evolution of the phenol concentration was followed through HPLC analysis (Agilent, 1200 Serie) using filtered aliquots ca. 2 ml of the suspension (Millipore Millex25 0.45 mm membrane filter).

Blank experiments were performed in the dark with catalyst as well as with illumination and no catalyst, and no changes in the initial concentration of phenol were observed in any of both cases.

3. Results and discussion

3.1. Characterisation

Fig. 1 shows XRD patterns of the fresh sample and after calcination treatment. As it can be seen, the sample is already crystalline